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RAIN REPELLENT

10 APRIL 1963

Prepared under
Navy, Bureau of Naval Weapons
CONTRACT NOw 62-0557-c

FINAL REPORT

FOSTER D. SNELL, INC.

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RAIN REPELLENT

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Contract NOw 62-0557-c

FINAL REPORT

This report applies to

work on Contracts

NOw 61-0463-c
NOas 60-6029-c

FOSTER D. SNELL, INC.
29 W. 15th St., N. Y., N. Y.

ABSTRACT

A rain repellent was developed, Formula 2911K-394, which is packaged in aerosol containers. Spraying of the repellent into the wind-stream hitting the windshield under rain conditions forms a coating which provides visibility.

Application of the repellent to a dry panel and treatment with a solution of p-toluene sulfonic acid in alcohol results in a film having good life when subjected to rain spray and resistance to both jet fuel and isopropyl alcohol.

The use of 10 centistoke methyl silicone oil, as contained in Formula 2911K-394, produces a film having improved resistance to jet fuel.

Table of Contents

I. SUMMARY

A. ENTIRE PROJECT

This is the final report to the Bureau of Naval Weapons under Contract NOw 62-0557-c on the development of a new and improved rain repellent for use on the glass windshields of high-speed aircraft not equipped with windshield wipers.

Recommendations are made for the use of Formula 2911K-394. This is a liquid repellent based on a silicone-titanium copolymer. The silicone-titanium copolymer is prepared by adding one part tetrabutyltitanate to two parts of the hydrolysis product of acidified dimethyldiethoxysilane and refluxing for two hours, the pot temperature being controlled within a range of 100-105°C. To 30 parts by volume of the silicone-titanium copolymer are added 20 parts by volume of 10 centistoke methyl silicone oil and 10 parts by volume of mineral spirits. The rain repellent is packaged as an aerosol with Freon 12 as the propellent in the proportion of 2 parts by volume of active material to 3 parts by volume of propellent.

The use of surfactants incorporated in acidified dimethyldiethoxysilane did not improve repellency under rain conditions.

Certain proprietary gels containing phosphates of titanium were not found useful as rain repellents either alone or in combination with acidified dimethyldiethoxysilane.

The use of mutual solvents for water and acidified dimethyldiethoxysilane did not improve application during rain conditions.

Silicone-titanium copolymers were produced which were found to coat the entire test panel under rain conditions and provide visibility.

Stability in storage was found to be greater for the silicone-titanium copolymer alone or in solution in mineral spirits than with combinations of silicone-titanium copolymer and dimethyldiethoxysilane.

A saturated solution of p-toluene sulfonic acid was found effective as a catalyst for the silicone-titanium copolymer alone and in solution in mineral spirits when applied to a dry panel pre-flight. Its stability on storage was found to be greater than that of sodium bisulfate in paste form.

B. FOURTH QUARTER

The addition of 10 centistoke methyl silicone oil to the silicone-titanium copolymer was found to improve resistance to jet fuel and to high temperature exposure.

Formula 2911K-394, containing 30 parts by volume of silicone-titanium copolymer, 20 parts by volume of 10 centistoke methyl silicone oil and 10 parts by volume of mineral spirits, packaged as an aerosol with Freon 12 as the propellent in the proportion of 2 parts by volume of active material to 3 parts by volume of propellent, was found to be stable after 4 months' exposure to a temperature of 160°F.

The use of ethyl silicate was not found advantageous in rain repellents for in-flight application during rain either in the form of a copolymer with dimethyldiethoxysilane or in mutual solution with it.

Formula 2911K-394 was found to be stable on storage. After exposure to a temperature of 160°F. for four months rain repellence both pre-flight and in-flight during rain conditions was undiminished.

As a catalyst for use with Formula 2911K-394 on a dry panel pre-flight a 70 per cent solution of p-toluene sulfonic acid in alcohol (Formula 2911K-353A) was found preferable to the 75 per cent solution previously used because of greater ease of preparation.

The use of an alkaline catalyst in conjunction with the silicone-titanium copolymer for pre-flight application did not result in repellent films.

II. INTRODUCTION

The purpose of this project was to develop a new and improved rain repellent suitable for use on the glass windshields of high-speed aircraft not equipped with windshield wipers. The work was concerned with, but not restricted to, complex haloid silanes.

(1) The material shall be suitable for application on the glass of pilot's enclosures, and it shall maintain satisfactory visibility through the glass during varying rain conditions.

(2) The applied material shall not produce an objectionable glare under varying conditions of light intensity.

(3) The treated surface shall have suitable characteristics so that visibility through the glass is maintained for a minimum of one (1) hour when the repellent is applied in liquid or gaseous form during flight.

(4) The rain repellent shall not have any adverse effects on the materials used in aircraft construction; such as aluminum, aluminum alloys, magnesium alloys, titanium and alloys, ferrous alloys, copper and alloys, aircraft finishes, rubber and elastomers, glass, etc.

(5) In view of the fact that the material is spread in film form, the rain repellent shall have suitable characteristics both in volume and when spread in a thin film.

(6) The material shall not be excessively high in cost.

(7) The material shall be non-flammable after application, and it shall have as high a flash point as possible (approximately 150°F. minimum) prior to application.

(8) The material shall be low in toxicity; that is, it shall not constitute a medical hazard to personnel or produce obnoxious vapors.

(9) The material shall possess good storage stability in the container; that is, it shall not deteriorate in the container under normal storage conditions in the temperature range of -10°F. to 160°F. for a period of one year.

(10) The material shall not, after application, attract or pick up excessive dust or light-weight particles.

(11) The material shall be ready-mixed for use.

(12) The material shall be capable of being applied by spraying, particularly during rain conditions.

(13) The material shall be capable of withstanding temperatures of -65°F. to 500°F. after application.

(14) The material shall be resistant to the common chemical compounds used in aircraft after application, particularly jet engine fuels and isopropyl alcohol.

The use of Formula 2911K-290 reported previously (Interim Report No. 3, dated 28 December 1962) gave a repellent film when sprayed under in-flight rain conditions and when spread over a dry panel in conjunction with an acid catalyst in pre-flight application. Continued investigation of the properties of this material revealed that resistance to jet fuel of the acid catalyzed film was deficient and that exposure of the film to a temperature of 500°F. also affected it adversely. Efforts were therefore made to improve these properties of the material. A study was undertaken of the value of the addition of silicone oils of varying viscosities to the silicone-titanium co-polymer contained in Formula 2911K-290.

It was considered that ethyl silicate, which is a tetrafunctional silicon ester similar to tetrabutyl titanate, a tetrafunctional titanium ester which has been successfully utilized in the preparation of silicone-titanium copolymers having useful properties as rain repellents for in-flight application, could behave in like fashion. During the last quarter copolymers of ethyl orthosilicate and dimethyldiethoxysilane hydrolysate were prepared and tested. Combinations of ethyl silicate and acidified dimethyldiethoxysilane were also investigated.

Storage stability tests were continued during the quarter. These included tests on repellents developed under the current contract as well as on Formula 2911H-2355, the repellent developed under the previous contract (NOw 61-0463-c). Twelve months' storage was completed by the latter rain repellent.

During the fourth quarter a further study was made of the catalysts for use with Formula 2911K-394 for pre-flight application. Both acid catalysts and alkaline catalysts were investigated and evaluated.

III. RECOMMENDATIONS

A. COMPOSITION

Repellent 2911K-394	Per Cent By Volume
Copolymer H	20.0
Methyl silicone oil (10 cs.)	13.3
Sovasol 5	6.7
Dichlorodifluoromethane	60.0

Catalyst 2911K-353A	Per Cent By Weight
p-Toluene sulfonic acid	70.0
Ethanol SD3A	30.0

Glass Cleaner 2911K-324	Per Cent By Weight
Sodium bisulfate (160 mesh)	70.0
Ethylene glycol	14.0
Cab-O-Sil M5	2.0
Water	14.0

B. RAW MATERIAL COSTS.

The following proportions are for the manufacture of 100 pounds of material. Prices given for raw materials are those of 15 March 1963 and are subject to change. Revisions may be necessary to arrive at costs on a delivered-to-plant basis.

Dimethyldiethoxysilane hydrolysate

Wt. (pounds)	Material	Cost/lb.	Cost/100 lbs. of Material
198.9	Dimethyldiethoxysilane	$ 3.40	$ 676.26
1.1	Sulfuric acid (96%)	0.15	0.165
80.0	Hexane	0.07	5.60
2.5	Sodium carbonate	0.14	0.35
183.2	Water	------	-----------
			$ 682.375

Raw Material Cost Per Pound = $ 6.83

Copolymer H

Wt. (pounds)	Material	Cost/lb.	Cost/100 lbs. of Copolymer
64.98	Dimethyldiethoxysilane hydrolysate	$ 6.83	$ 443.16
35.02	Tetra butyl titanate	1.30	45.53
			$ 488.69

Raw Material Cost Per Pound = $ 4.89

Formula 2911K-394 (Repellent)

Wt. (pounds)	Material	Cost/lb.	Cost/100 lbs. of Repellent
15.22	Copolymer H	$ 4.89	$ 74.43
10.00	Methyl silicone oil (10 cs.)	2.45	24.50
4.26	Sovasol 5	0.03	0.13
70.52	Dichlorodifluoromethane	0.28	19.75
			$ 118.81

Raw Material Cost Per Pound = $ 1.19

Formula 2911K-353A (Catalyst)

Wt. (pounds)	Material	Cost/lb.	Cost/100 lbs. of Catalyst
70.0	p-Toluene sulfonic acid	$ 0.83	$ 58.10
30.0	Ethanol SD3A	0.13	3.90
			$ 62.00

Raw Material Cost Per Pound = $ 0.62

Formula 2911K-324 (Cleaner)

Wt. (pounds)	Material	Cost/lb.	Cost/100 lbs. of Cleaner
70.0	Sodium bisulfate	$ 0.30	$ 21.00
2.0	Cab-O-Sil M-5	1.25	2.50
14.0	Ethylene glycol	0.18	2.52
14.0	Water	---	----
			$ 26.02

Raw Material Cost Per Pound = $ 0.26

C. METHOD OF MANUFACTURE

Copolymer H

The manufacture of Copolymer H requires a stoppered glass, or other acid resistant, reaction vessel fitted with a condenser and an acid resistant stirrer. A means of cooling the flask may also be required.

To 99.75 parts by volume of dimethyldiethoxysilane 0.25 part by volume of 96% sulfuric acid is added slowly with stirring. When the acidified dimethyldiethoxysilane has cooled to 70-80°F., 50 parts by volume of water are added slowly with slow stirring. An exothermic reaction occurs and the rate of water addition should be regulated so that the reaction temperature does not exceed 50°C. (122°F.). In manufacture on a small scale the water is added over a one hour period. After addition of all of the water 25 parts of a 4 per cent (weight/volume) solution of sodium carbonate in water are added to neutralize the acid catalyst. At this point stirring is stopped and the reaction mixture is allowed to cool to 70-80°F. The reaction mixture will separate into an upper oil phase and a lower aqueous phase.

When the reaction mixture has cooled, 50 parts by volume of hexane are added and the mixture stirred for a short time and the phases allowed to separate. The lower aqueous phase is discarded leaving a clear solution of hydrolysate in hexane. The residual hexane solution is heated to a pot temperature of 100-105°C. and hexane, ethanol and traces of water are

removed by distillation. The vapor temperature should not exceed 80°C. during this step. Approximately 50 parts of hydrolysate are obtained as a residue.

To 50 parts of hydrolysis product, cooled to 70-80°F., are added 25 parts by volume of tetra butyl titanate. Tetra butyl titanate is moisture sensitive and must be protected from atmospheric moisture to prevent hydrolysis and polymerization. The mixture is stirred slowly and refluxed at a pot temperature of 105°C. for 2 hours. A clear amber liquid copolymer is obtained.

Formula 2911K-394 (Repellent)

The manufacture of the active part of the rain repellent requires a glass or stainless steel container with a tight fitting cover and a stirrer. The repellent is prepared by combining 20.0 parts by volume of Copolymer H, 13.3 parts by volume of 10 centistoke methyl silicone oil and 6.7 parts by volume of Sovasol 5. The solution is packaged in aerosol cans and pressurized with dichlorodifluoromethane to form the completed formulation which contains 40 per cent by volume rain repellent and 60 per cent by volume propellent.

During preparation and packaging the solution must be protected from atmospheric moisture to prevent hydrolysis and polymerization. The solution is packaged in tin lined aerosol cans fitted with stainless steel valves in tin plated steel mounting cups.

Stainless steel valves such as S-32 valves made by Emson Research, Inc., Burr Court, Bridgeport, Conn. have been found satisfactory for use. Tin lined Spratainers, made by Crown Cork & Seal Co., Inc., Chicago, Illinois, have been used as the aerosol containers.

Formula 2911K-353A (Catalyst)

The manufacture of the catalyst requires a closed glass or other acid resistant container fitted with an acid resistant stirrer. To 70 parts by weight of p-toluene sulfonic acid, practical, are added 30 parts by weight of Ethanol SD3A. The mixture may be heated to increase the rate of solution of the acid in the alcohol. The solution should be protected from moisture during preparation and packaging. The catalyst should be packaged in glass bottles with tight fitting caps with polyethylene seals or a piece of polyethylene film should be used to prevent contact between the catalyst and the cap.

Formula 2911K-324 (Cleaner)

The manufacture of the glass cleaner requires a pebble mill or other acid resistant grinder to reduce the technical granular sodium bisulfate to a fine powder of approximately 160-180 mesh.

The glass cleaner is manufactured in a glass or other acid resistant container fitted with an acid resistant stirrer. Fourteen parts by weight of ethylene glycol and water, respectively, are combined and 2 parts by weight of Cab-O-Sil M-5 added slowly with stirring. The mixture is stirred until all of the Cab-O-Sil is dispersed. Seventy parts by weight of the powdered sodium bisulfate are added slowly with stirring until a smooth paste is obtained. The paste is thixotropic. It is recommended that the cleaner mixture be stirred during the filling operation to insure a homogeneous product. The cleaner should be packaged in glass jars with tight fitting caps with polyethylene liners or a piece of polyethylene film should be used to prevent contact between the cleaner and the cap.

D. RESULTS OF TESTS:

1. Rain Spray Test

Formula 2911K-394

a. Pre-flight application catalyzed with Catalyst 2911K-353A

1. at room temperature	over 1 hour
2. after heating for 1 hour at 500°F.	1 hour
3. after exposure for 24 hours at -65°F.	over 1 hour
4. after exposure to jet fuel	1 hour
5. after exposure to isopropyl alcohol	over 1 hour

b. In-flight application

1. Rain conditions	2 minutes

2. Roll Angle (MIL-K-6882A) 10°

3. Flash Point (Tag Open Cup)

Repellent 2911K-394	85°F.
Catalyst 2911K-353A	100°F.
Cleaner 2911K-324	None

4. Flammability of Aerosol Package Formula 2911K-394

Tested in accordance with I. C. C. Tariff No. 10.

(a) Open Drum	Passes
(b) Closed Drum	
Top	Passes
Side	Passes
Bottom	Passes
(c) Flame projection 12 inches	Passes

D. RESULTS OF TESTS: (Cont'd.)

5. Application of Film (Pre-Flight)

	Temperature	Application	Polishing	Film	Rain Spray
a.	40°F.	Easy	Easy	Clear	1 hour
b.	75°F.	Easy	Easy	Clear	1 hour +
c.	120°F.	Easy	Easy	Clear	1 hour +
d.	140°F.	Easy	Easy	Clear	1 hour +

6. Effect on Aircraft Materials

a. Corrosion of Metals

Metal coupons 1 inch x 6 inches x 0.050 inches were sprayed with Formula 2911K-394 and allowed to stand 24 hours at 70°F.

Metal	Change in Weight (grams)	Observation
Steel 4130	+ 0.0004	No effect.
Aluminum 2S	+ 0.0012	No effect.
Aluminum 24ST	+ 0.0002	No effect.
Magnesium FSI	+ 0.0012	No effect.
Copper	+ 0.0012	No effect.
Titanium RC-70	+ 0.0006	No effect.

D. RESULTS OF TESTS: (Cont'd.)

6. Effect on Aircraft Materials (Cont'd.)

b. Crazing of Acrylic Plastics

(Method 3053.1 of Specification LP-406B as modified by Specification MIL-K-6882A).

Repellent 2911K-394	No effect.
Catalyst 2911K-353A	No effect.
Cleaner 2911K-324	No effect.

c. Effect on Aircraft Finishes

Six coated aluminum test panels, 3 inches by 6 inches, were tested for resistance to the repellent in accordance with Specification MIL-D-7946A.

Coating		Observation
Light Gull Gray (No. 620)	MIL-L-15938	No effect
Dark Gull Gray (No. 621)	MIL-L-15938	No effect
Olive Drab	MIL-L-5556	No effect
Seaplane Gray	MIL-L-7178	No effect
White	MIL-L-7178	No effect
Blue	MIL-E-7729	No effect

E. METHOD OF APPLICATION

For In-Flight Application (under rain conditions).

No preliminary treatment of windshield is required.

1. Spray a heavy coat of the repellent into the airstream hitting the windshield.
2. Spray the windshield with a light coat of repellent as required to maintain visibility.

For Pre-Flight Application.

1. Clean windshield with glass cleaner by rubbing, using a clean tissue and working over the windshield until the paste wets the surface.
2. Remove the dried cleaner with a clean tissue and wash the windshield with water, if available. Spots which do not wet should be recleaned.
3. Dry and polish the windshield with a clean tissue.
4. Fold a tissue into a pad about 2 inches square, wet the pad with the Catalyst, Formula 2911K-353A, and rub over the windshield leaving a film of Catalyst on the surface.
5. To coat the windshield with the repellent hold the aerosol can about 6 inches from the surface and spray with a fanning motion, starting at the top and wetting the entire windshield.

E. METHOD OF APPLICATION (Cont'd.)

6. Allow the coated windshield to air dry about 1 minute at normal temperatures (70°-80°F.) and 3 minutes at lower temperatures (30°-40°F.).

7. Polish the coated windshield with the tissue wetted with the Catalyst rubbing briskly over all of the surface.

8. Polish with a clean tissue - a final brisk polish will remove any residual greasiness.

9. To recoat repeat steps 1-8.

Note: Clean soft cloths such as terry cloth, if available, should be substituted for the cleaning tissues.

F. SOURCES OF RAW MATERIALS

Dimethyldiethoxysilane L-45 Silicone Oil (10 centistokes)	Silicones Division Union Carbide Corp. 270 Park Avenue New York 17, New York
Sulfuric Acid (96%) Sodium carbonate, U.S.P.	J. T. Baker Chemical Co. Phillipsburg, New Jersey
Hexane (commercial grade)	American Mineral Spirits Co. Mountain Avenue Murray Hill, New Jersey
Tetrabutyl titanate	Organic Chemicals Dept. E. I. du Pont de Nemours & Co., Inc. Wilmington 98, Delaware
Sovasol 5	Socony Mobil Oil Co., Inc. 150 East 42nd Street New York, New York
Dichlorodifluoromethane (Freon 12)	Freon Products Div. E. I. du Pont de Nemours & Co., Inc. Wilmington 98, Delaware
p-Toluene sulfonic acid (96%), practical	Eastman Organic Chemical Co. Rochester 3, New York

F. SOURCES OF RAW MATERIALS (Cont'd.)

Ethanol SD3A Ethylene glycol	Union Carbide Chemicals Co. 270 Park Avenue New York 17, New York
Sodium bisulfate (granular, technical)	Fisher Scientific Company 635 Greenwich Street New York 14, New York
Cab-O-Sil M-5	Godfrey L. Cabot, Inc. 125 High Street Boston 10, Massachusetts

IV. USE OF SILICONE OILS IN CONJUNCTION WITH SILICONE-TITANIUM COPOLYMERS

In Interim Report No. 3, dated 28 December 1962, Formula 2911K-290 was reported to form a repellent film when sprayed on a wet panel under in-flight rain conditions and when spread over a clean dry panel in conjunction with an acid catalyst in pre-flight application. During the present quarter investigation of this formulation was continued. Storage stability of the aerosol packaged repellent and resistance of the pre-flight applied film to contamination and exposure to high temperature were evaluated.

During the course of the investigation of Formula 2911K-290, a 50 per cent solution of silicone-titanium Copolymer H in Sovasol 5 and pressurized with Freon 12, it was found that the storage stability of the repellent was good. After six weeks' storage at 160°F. no decrease in film forming ability was observed when the film was applied and acid catalyzed pre-flight or when applied during in-flight rain conditions. The exposure of pre-flight applied films to a temperature of 500°F. for one hour before testing resulted in a decrease in rain spray life from one hour, for an unheated panel, to three-quarters of an hour. The investigation also disclosed that the Formula 2911K-290 film had poor resistance to simulated jet fuel. Rain spray lives

of five to thirty minutes were obtained when pre-flight coated panels were contaminated with jet fuel prior to testing on the rain spray test apparatus. Isopropyl alcohol contamination caused no decrease in rain spray life. The poor jet fuel resistance and reduced rain spray life after exposure at 500°F. are probably due to incomplete decomposition of Copolymer H by the acid catalyst during the pre-flight application. While the acid catalyzed film has a good normal rain spray life, it is sufficiently soluble in the jet fuel for contamination with this material to cause a marked reduction in rain spray life. The reduction in rain spray life after exposure at 500°F. is probably due to oxidation of the film, which is also an indication of incomplete decomposition of the silicone-titanium copolymer by the acid catalyst. If the copolymer were completely decomposed into silicone fragments bonded to the glass and a mixture of titanium compounds which are removed by polishing the panel, then subsequent baking of the panel should have no deleterious effect on the film. It has been reported earlier that films formed by Formula 2911K-2157E, acidified dimethyldiethoxysilane, are not damaged by exposure to a temperature of 500°F. and that durable repellent films can be obtained by coating the test panel with a silicone oil and baking the coated test panel. Similar results would be expected from the film deposited by the acid catalysis of Copolymer H if the decomposition were complete.

In an attempt to increase the resistance to the action of jet fuel, Formula 2911K-290 was modified by the addition of silicone oils. The oils, polydimethylsiloxanes, are stable in neutral media, have good high temperature stability and can be catalyzed to form films having good rain spray resistance. Previous attempts to combine Copolymer H with dimethyldiethoxysilane to form a dual purpose repellent were unsuccessful because of poor high temperature storage stability (Formula 2911K-291, Interim Report No. 3).

During the course of the investigation it was found that the durability of the pre-flight films was dependent to some extent on the application technic. It was found that the jet fuel resistance of the films increased when the repellent was allowed to react with the catalyst for a short time before polishing the coated panel. As a result, the following standard application procedure was adopted.

(1) Catalyst 2911K-353A was applied to a clean test panel with a tissue.

(2) The catalyst coated panel was sprayed with a heavy coat of the repellent to be tested.

(3) The coated panel was allowed to stand at room temperature for 1 minute.

(4) The coated panel was polished with the catalyst wetted tissue until the panel felt oily or slippery.

(5) The panel was polished with a clean tissue until clear.

Section IX, Table I lists formulations containing Formula 2911K-290 modified by the replacement of part of the solvent, Sovasol 5, by Union Carbide L-45 Silicone Oils. Oils of ten to five hundred centistoke viscosity were used in the effort to increase the resistance of the pre-flight applied film to jet fuel contamination and high temperature exposure.

In general the best results were obtained with the lowest viscosity oil (10 centistokes). Formula 2911K-391 to 396, a series of repellents containing from 3.3 per cent to 20.0 per cent 10 centistoke silicone oil, all have good in-flight film forming properties and rain spray lives of one hour after jet fuel contamination of the film formed by pre-flight application. Formulas 2911K-391 and 392, which contain 3.3 per cent and 6.7 per cent of 10 centistoke oil respectively, had rain spray lives of one hour after jet fuel contamination when large amounts of repellent were applied and the coated panels were carefully polished. When the concentration of silicone oil was increased to 10 per cent or more (Formulas 2911K-393 to 396) the application technic became less critical. The films of the latter formulations are easily applied and have rain spray lives of one hour after contamination by jet fuel. Films formed by in-flight application are clear, coat the entire test panel and have rain spray lives of at least 2 minutes before wetting begins. Formula 2911K-396, which contains 20.0 per cent of the 10 centistoke oil, has a relative disadvantage in that the excess repellent applied in flight, does not flow or sweep across the test panel as readily as with formulations containing less silicone oil. Formula 2911K-394 was determined to have the best overall properties of this series. Panels coated with Formula 2911K-394 and catalyzed by Formula 2911K-353A, were heated to 500°F. for one hour and tested on the rain spray test apparatus. A rain spray life of one hour was obtained.

Formulas 2911K-397, 402 and 403 each contain 20 centistoke silicone oil. Formulas 2911K-397 and 402, which contain 3.3 per cent and 6.7 per cent silicone oil respectively, had rain spray lives of 1 hour after jet fuel contamination. When the concentration of silicone oil was increased to 13.3 per cent in Formula 2911K-403, the jet fuel resistance was reduced and a rain spray life of 3/4 hour was obtained. The rain spray life of the film applied in flight was only one minute and the movement of the excess repellent across the test panel was slower than with Formula 2911K-394, which contains an equal amount of 10 centistoke oil.

When 50 centistoke oil was used in Formulas 2911K-404 and 405, one hour rain spray lives were obtained after jet fuel contamination, but the movement of the excess repellent applied during in-flight rain conditions was slow.

Repellent formulations containing higher viscosity oils had poorer rain spray lives after jet fuel contamination. When 100, 350 or 500 centistoke oils were used (Formulas 2911K-399 to 401 and 2911K-406 to 408) jet fuel contamination reduced the rain spray life to approximately one half hour. In addition the movement of the excess repellent across the test panel during in-flight rain conditions was slow.

Formula 2911K-394 has the best overall properties of the formulations tested. The acid catalyzed pre-flight applied film has a rain spray life of one hour after jet fuel contamination and after heating at 500°F. for one hour. The film formed during in-flight rain conditions has a rain spray life of 2 minutes before wetting begins and the excess repellent moves quickly across

the test panel. No change in properties was noted when this formulation was tested after 4 months' storage at 160°F.

V. STORAGE STABILITY OF AEROSOL PACKAGES

The investigation of the storage stability of aerosol packaged rain repellents was continued during the present quarter. The effect of storage at room temperature and at 160°F. was evaluated by testing the aged formulations on the rain spray test apparatus periodically. The aerosol packages were prepared using tinplate Spratainers made by Crown Cork and Seal Co., Inc., Chicago, Illinois and S-32 stainless steel aerosol valves in tinplate mounting cups with polyethylene dip tubes and S-1 spray buttons. The valves and spray buttons are made by Emson Research, Inc., Burr Court, Bridgeport, Conn.

In addition to the repellents, samples of Catalyst 2911K-353A were aged in glass bottles at 160°F. and at room temperature. The effect of ageing was evaluated by using the catalyst in conjunction with Formula 2911K-394 in pre-flight applications. The following table lists the formulations tested.

Formula No.	Storage Time	Storage Temp.	Rain Spray Life Pre-flight	Rain Spray Life Jet Fuel	Rain Spray Life In-flight	Comments
2911K-290	5 months	70°F.	1 hour	---	2 minutes	Pre-flight applications were catalyzed with Catalyst 2911K-353A aged 3 months at 160°F.
2911K-290	5 months	160°F.	1 hour	---	2 minutes	
2911K-292	5 months	160°F.	1 hour	---	2 minutes	
2911K-379	5 months	160°F.	---	---	2 minutes	
2911K-394	4 months	70°F.	1 hour	1 hour	2 minutes	
2911K-394	4 months	160°F.	1 hour	1 hour	2 minutes	
2911H-2355	12 months	70°F.	1 hour	---	---	---
2911H-2355	12 months	160°F.	3/4 hour	---	---	---

Formula 2911K-394, the recommended formulation, shows no decrease in rain repellent properties after 4 months' storage at room temperature or at 160°F. Formulas 2911K-290 and 292, solutions of Copolymer H in Sovasol 5, are stable after 5 months' storage at 160°F. Formula 2911K-379, a combination of Copolymer H and propellent, formed a clear film with a rain spray life of 2 minutes when applied during in-flight rain conditions after 5 months' ageing at 160°F. Althought these formulations, 2911K-290, 292 and 379, are not considered for use because of poor resistance to jet fuel when used in an acid catalyzed pre-flight application, they demonstrate the stability of Copolymer H at 160°F. No stoppage or malfunction has developed in the aerosol valves and none of the cans show any evidence of leakage.

The pre-flight catalyst, Formula 2911K-353A, shows no decrease in catalytic ability after 3 months' storage in glass bottles at 160°F. Some darkening of the solution was observed and some attack on the cap liner. For this reason caps with polyethylene liners or the use of polyethylene film to prevent contact between the acid solution and the cap is recommended.

Formula 2911H-2355, an aerosol packaged repellent based on acidified dimethyldiethoxysilane, was evaluated after 12 months' storage. This formulation was developed under Contract NOw 61-0463-c and was recommended in the Final Report dated 10 January 1962. Samples retained when the 100 kits were submitted in conformance with the contract were found to have a rain spray life of 1 hour after 12 months' storage at room temperature. None

of the cans showed any evidence of leakage or significant loss of propellent during storage. One valve malfunctioned on the first use after storage. The valve stem remained depressed and had to be closed by lifting the spray button and stem by hand. Subsequent use of this package did not result in malfunction.

Samples of Formula 2911H-2355 show a slight decrease in rain spray resistance after 12 months' storage at 160°F. Rain spray lives of 3/4 hour were obtained. Wetting of the film is caused by soil build up on the panel and the film can be restored by wiping the test panel with a tissue.

The aerosol cans and valves used with Formula 2911H-2355 were coated in the laboratory with an acid resistant phenolic-epoxy coating (Formula 2911H-2268, Interim Report No. 3 under the above contract, dated 10 October 1961). From the results of these tests it appears that the coating is sufficiently acid resistant for 1 years' storage at room temperature.

Although samples of aerosol packaged rain repellents have been found to have a satisfactory rain spray resistance after storage at 160°F., high temperature storage of the containers is not recommended. Generally, aerosol packages suffer some loss of propellent on long term storage and high temperatures would increase the propellent loss due to increased package pressure.

VI. INVESTIGATION OF ETHYL SILICATE FOR USE IN RAIN REPELLENTS

During the last quarter the investigation of ethyl orthosilicate for use in rain repellent formulations was begun. Ethyl silicate is a tetrafunctional silicon ester similar to tetrabutyl titanate, a tetrafunctional titanium ester which has been used successfully in the preparation of silicone-titanium copolymers utilized as rain repellents. For this purpose combinations of ethyl silicate and acidified dimethyldiethoxysilane were evaluated and copolymers of ethyl silicate and dimethyldiethoxysilane hydrolysate were prepared and tested.

A. PREPARATION OF COPOLYMERS

The dimethyldiethoxysilane-ethyl silicate copolymers were prepared according to the methods described in previous reports under the present contract for the preparation of silicone-titanium copolymers.

A. PREPARATION OF COPOLYMERS (Cont'd.)

Copolymer T_1

To 100 milliliters of dimethyldiethoxysilane containing 0.25 milliliter of concentrated sulfuric acid 50 milliliters of water were added slowly with stirring. An exothermic reaction occurred and on continued addition of water a silicone oil phase separated. After addition of all of the water, 25 milliliters of a 4 per cent solution of sodium carbonate in water were added to neutralize the acid. The oil layer was extracted with 50 milliliters of hexane and the hexane solution of the hydrolysate was heated to a pot temperature of 100°-105°C. and hexane, ethanol and water removed by distillation. One-hundred milliliters of hydrolysis product were obtained as a residue.

To 100 milliliters of hydrolysis product were added 40 milliliters of tetraethyl orthosilicate. The reaction mixture was heated for 2 hours at a pot temperature of 105°C. The reaction mixture did not reflux at this temperature. A colorless liquid copolymer was obtained.

Copolymer T_2

Copolymer T_2 was prepared by refluxing Copolymer T_1 at a pot temperature of 150°C. for 2 hours. A pale yellow copolymer was obtained.

Copolymer T_3

Copolymer T_3 was prepared by refluxing Copolymer T_1 for 5 hours at a pot temperature of 150°C. A pale yellow copolymer was obtained.

Copolymer T_4

To 100 parts of the hydrolysate, obtained as described above under Copolymer T_1, 40 parts of ethyl silicate were added and the reaction mixture refluxed for 12 hours at a pot temperature of 150°C. A pale yellow copolymer was obtained.

B. EVALUATION OF ETHYL SILICATE FORMULATIONS

In a series of experiments the effect of the addition of ethyl silicate to acidified dimethyldiethoxysilane was investigated. Dimethyldiethoxysilane containing 0.25 per cent by volume of concentrated sulfuric acid forms a durable repellent film when applied to a clean dry windshield (Formula 2911H-2157E, Final Report, Contract NOas 60-6029-c, dated 20 January 1961). Efforts to apply this formulation to a wet test panel on the rain spray test apparatus during in-flight rain conditions have been unsuccessful. Ethyl silicate can be hydrolyzed in an acid medium to form hydrated silica similar to the hydrolysis of tetrabutyl titanate to yield titanium dioxide. It was hoped that the cohydrolysis of acidified dimethyldiethoxysilane and ethyl silicate would yield an adherent repellent film when applied in flight.

Formulas 2911K-410 to 414, 418 and 423, Section IX, Table II, are solutions of ethyl silicate in acidified dimethyldiethoxysilane. Formula 2911K-410, which contains 1 per cent ethyl silicate, has a rain spray life of one hour after jet fuel contamination when applied to a dry panel pre-flight. A repellent film was not obtained when the material was applied during in-flight rain conditions using a Jet-Pak Sprayer, a self pressurized spray kit similar to that described in Specification MIL-S-22805, dated 17 January 1961. No improvement was noted when this formulation was packaged in an aerosol container with Freon 12 as the propellent (Formula 2911K-418). In both cases the point of impact was not coated, but some repellency developed on the edges

of the panel. In Formula 2911K-423 the concentration of sulfuric acid was increased to 0.5 per cent. A slight improvement in the in-flight film was obtained, but only the edges of the test panel were coated.

When the concentration of ethyl silicate was increased in Formulas 2911K-411 to 414, the pre-flight applications resulted in greasy films which were difficult to polish and had reduced rain spray lives. No improvement in the in-flight film forming ability was obtained.

When ethyl silicate was combined with dimethyldiethoxysilane hydrolysate in Formulas 2911K-415 and 419, some repellency was obtained on the edges of the panel when the repellent was applied under in-flight rain conditions. When Formula 2911K-415 was applied to a dry panel and treated with the catalyst, Formula 2911K-353A, a rain spray life of 5 minutes was obtained.

Formulas 2911K-416 and 417 are solutions of silicone Copolymers T_1 and T_2, respectively, in Sovasol 5 and pressurized with Freon 12. Application of these repellents during in-flight rain conditions resulted in the formation of resinous deposits on the edges of the panel and repellent films were not formed at the point of impact. Similar results were obtained when Formula 2911K-428, a 50 per cent solution of Copolymer T_1 in acidified ethanol, was applied in-flight with a Jet-Pak Sprayer.

Pre-flight application of this repellent gave a film with a rain spray life of one hour. This is indirect evidence that heating ethyl silicate with dimethyldiethoxysilane hydrolysate caused a reaction to take place, since Formula 2911K-415, a solution of the starting materials, had a rain spray life of only 5 minutes in an acid catalyzed pre-flight application. Formulas 2911K-430 and 431, Copolymers T_3 and T_4 respectively, also form films with good

rain spray resistance when used in acid catalyzed pre-flight applications.

In-flight application of formulations containing Copolymers T_3 and T_4 do not form repellent films (Formulas 2911K-429 to 431A). Some repellency develops on the edges of the test panel, but the point of impact and the center of the test panel are not coated.

None of the formulations containing ethyl silicate have the combination of properties necessary for a repellent for in-flight application.

VII. STUDY OF CATALYSTS

Formula 2911K-353, a saturated solution of p-toluene sulfonic acid in ethanol, was reported in Interim Report No. 3 as an effective catalyst for the pre-flight application of repellent films. During the last quarter the investigation of acid catalysts to be used in conjunction with the repellent, Formula 2911K-394, was continued. In addition the incorporation of alkaline catalysts in the repellent formulation to catalyze it for pre-flight application was studied.

In Formula 2911K-353A, a modification of Formula 2911K-353, the concentration of p-toluene sulfonic acid was reduced to 70 per cent and the ethanol content increased. The purpose of this change was to facilitate the preparation of the catalyst. Formula 2911K-353 is a saturated solution of the acid in ethanol and the slight change in the proportions of the components increases the ease of solution of the acid in the ethanol. When Formula 2911K-353A is used as the catalyst in conjunction with Formula 2911K-394 or with dimethyldiethoxysilane (unacidified), the rain spray lives of the films are at least one hour. The flash point of Formula 2911K-353A is 100°F., Tag Open Cup.

Ethanol was replaced by isopropanol (99 per cent) in Formula 2911K-353B in an attempt to obtain a catalyst solution having a higher flash point. It was found that p-toluene sulfonic acid was less soluble in isopropanol. A saturated solution contains only 60 per cent of the acid and the flash point of the solution is 90°F., Tag Open Cup. In Formulas 2911K-353C and 353D water was added to the saturated alcoholic solutions of p-toluene sulfonic acid in attempts to increase the flash point. The addition of water to the catalyst decreased the catalytic ability of the p-toluene sulfonic acid in both formulations.

Formula 2911K-353A, a solution containing 70 per cent p-toluene sulfonic acid in ethanol was found to be the most suitable acid catalyst for the pre-flight film application.

The incorporation of an alkaline catalyst in the repellent formulation was also investigated during the final quarter. The effect of alkali on the stability of Copolymer H was evaluated in Formulas 2911K-420, 421 and 424 to 427. These are alcoholic solutions of Copolymer H containing potassium hydroxide as a catalyst for pre-flight film application. On preparation all of the formulations were stable and showed no evidence of decomposition of Copolymer H. After standing at room temperature for one week Formula 2911K-420, a 50 per cent solution of Copolymer H in ethanol containing 5 per cent potassium hydroxide, increased in viscosity. Under the same conditions Formula 2911K-421, a 50 per cent solution of Copolymer H in butanol containing 2.5 per cent potassium hydroxide, gelled. Solutions containing less alkali appear to be more stable. None of the formulations tested formed a repellent film when used in a pre-flight application.

VIII. CONCLUSIONS

1. A rain repellent was developed, Formula 2911K-394, which can be applied in flight during rain to form a coating on the windshield which provides visibility. When applied to the windshield preflight in conjunction with a catalyst, a rain repellent coating is formed which is resistant to the action of jet fuel, isopropyl alcohol and temperatures of −65°F. to 500°F.

2. The addition of 10 centistoke methyl silicone oil to the silicone-titanium copolymer, as contained in Formula 2911K-394, results in improved resistance of the film to jet fuel.

Respectfully submitted,

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IX. RESULTS OF TESTS

(Tables I, II and III)

Table I. - Silicone-Titanium Copolymer Repellents Containing Silicone Oils

Formula 2911K-	Composition	Per Cent By Volume	Rain Spray Life: Pre-flight	Rain Spray Life: Jet Fuel	Rain Spray Life: In-flight Applic.	Comments
391	Copolymer H	20.0	1 hr. +	1 hr.	2 min.	
	Silicone oil, 10 cs.	3.3				
	Sovasol 5	16.7				
	Freon 12	60.0				
392	Copolymer H	20.0	1 hr. +	1 hr.	2 min.	
	Silicone oil, 10 cs.	6.7				
	Sovasol 5	13.3				
	Freon 12	60.0				

Table I. (Cont'd.)

Formula 2911K-	Composition	Per Cent By Volume	Rain Spray Life: Pre-flight	Rain Spray Life: Jet Fuel	Rain Spray Life: In-flight Applic.	Comments
393	Copolymer H	20.0	1 hr. +	1 hr.	2 min.	
	Silicone oil, 10 cs.	10.0				
	Sovasol 5	10.0				
	Freon 12	60.0				
394	Copolymer H	20.0	1 hr. +	1 hr.	2 min.	
	Silicone oil, 10 cs.	13.3				
	Sovasol 5	6.7				
	Freon 12	60.0				
395	Copolymer H	20.0	1 hr. +	1 hr.	2 min.	
	Silicone oil, 10 cs.	16.7				
	Sovasol 5	3.3				
	Freon 12	60.0				
396	Copolymer H	20.0	1 hr. +	1 hr.	2 min.	
	Silicone oil, 10 cs.	20.0				
	Freon 12	60.0				

Table I. (Cont'd.)

Formula 2911K-	Composition	Per Cent By Volume	Rain Spray Life: Pre-flight	Rain Spray Life: Jet Fuel	Rain Spray Life: In-flight Applic.	Comments
397	Copolymer H	20.0	1 hr.	1 hr.	2 min.	
	Silicone oil, 20 cs.	3.3				
	Sovasol 5	16.7				
	Freon 12	60.0				
398	Copolymer H	20.0	3/4 hr.	15 min.	2 min.	
	Silicone oil, 50 cs.	3.3				
	Sovasol 5	16.7				
	Freon 12	60.0				
399	Copolymer H	20.0	1 hr.	3/4 hr.	2 min.	
	Silicone oil, 100 cs.	3.3				
	Sovasol 5	16.7				
	Freon 12	60.0				
400	Copolymer H	20.0	1 hr.	30 min.	2 min.	
	Silicone oil, 350 cs.	3.3				
	Sovasol 5	16.7				
	Freon 12	60.0				

Table I. (Cont'd.)

Formula 2911K-	Composition	Per Cent By Volume	Rain Spray Life: Pre-flight	Rain Spray Life: Jet Fuel	Rain Spray Life: In-flight Applic.	Comments
401	Copolymer H	20.0	1 hr.	30 min.	2 min.	
	Silicone oil, 500 cs.	3.3				
	Sovasol 5	16.7				
	Freon 12	60.0				
402	Copolymer H	20.0	---	1 hr.	2 min.	
	Silicone oil, 20 cs.	6.7				
	Sovasol 5	13.3				
	Freon 12	60.0				
403	Copolymer H	20.0	---	3/4 hr.	1 min.	
	Silicone oil, 20 cs.	13.3				
	Sovasol 5	6.7				
	Freon 12	60.0				
404	Copolymer H	20.0	---	1 hr.	1 min.	
	Silicone oil, 50 cs.	6.7				
	Sovasol 5	13.3				
	Freon 12	60.0				

Table I. (Cont'd.)

Formula 2911K-	Composition	Per Cent By Volume	Rain Spray Life: Pre-flight	Rain Spray Life: Jet Fuel	Rain Spray Life: In-flight Applic.	Comments
405	Copolymer H	20.0	---	1 hr.	2 min.	
	Silicone oil, 50 cs.	13.3				
	Sovasol 5	6.7				
	Freon 12	60.0				
406	Copolymer H	20.0	---	30 min.	2 min.	
	Silicone oil, 100 cs.	6.7				
	Sovasol 5	13.3				
	Freon 12	60.0				
407	Copolymer H	20.0	---	20 min.	2 min.	
	Silicone oil, 350 cs.	6.7				
	Sovasol 5	13.3				
	Freon 12	60.0				
408	Copolymer H	20.0	---	30 min.	2 min.	
	Silicone oil, 500 cs.	6.7				
	Sovasol 5	13.3				
	Freon 12	60.0				

Table II. - Ethyl Silicate In Rain Repellents

Formula 2911K.	Composition	Per Cent By Volume	Rain Spray Life: Pre-flight	Rain Spray Life: Jet Fuel	Rain Spray Life: In-flight Applic.	Comments
410	Ethyl silicate Dimethyldi-ethoxysilane (acidified)	1.0 99.0	1 hr. +	1 hr.	---	
411	Ethyl silicate Dimethyldi-ethoxysilane (acidified)	2.0 98.0	15-30 min.	---	Nil	Greasy film.
412	Ethyl silicate Dimethyldi-ethoxysilane (acidified)	5.0 95.0	15 min.	---	Nil	Greasy film.

Table II. (Cont'd.)

Formula 2911K-	Composition	Per Cent By Volume	Rain Spray Life: Pre-flight	Rain Spray Life: Jet Fuel	Rain Spray Life: In-flight Applic.	Comments
413	Ethyl silicate Dimethyldi-ethoxysilane (acidified)	10.0 90.0	15 min.	---	Nil	Greasy film.
414	Ethyl silicate Dimethyldi-ethoxysilane (acidified)	16.7 83.3	10 min.	---	Nil	
415	Ethyl silicate Dimethyldi-ethoxysilane hydrolysate	28.6 71.4	5 min.	---	Nil	
416	Copolymer T_1 Sovasol 5 Freon 12	20.0 20.0 60.0	---	---	Nil	

Table II. (Cont'd.)

Formula 2911K-	Composition	Per Cent By Volume	Rain Spray Life: Pre-flight	Rain Spray Life: Jet Fuel	Rain Spray Life: In-flight Applic.	Comments
417	Copolymer T_2	20.0	---	---	Nil	
	Sovasol 5	20.0				
	Freon 12	60.0				
418	Ethyl silicate	0.2	1 hr.	1 hr.	Nil	
	Dimethyldi-ethoxysilane (acidified)	19.8				
	Sovasol 5	20.0				
	Freon 12	60.0				
419	Ethyl silicate	6.0	---	---	Nil	
	Dimethyldi-ethoxysilane hydrolysate	14.0				
	Sovasol 5	20.0				
	Freon 12	60.0				
423	Ethyl silicate	1.0	1 hr. +	---	Nil	
	Dimethyldi-ethoxysilane	98.5				
	Sulfuric acid (96%)	0.5				

Table II. (Cont'd.)

Formula 2911K-	Composition	Per Cent By Volume	Rain Spray Life: Pre-flight	Rain Spray Life: Jet Fuel	Rain Spray Life: In-flight Applic.	Comments
428	Copolymer T_1 Sulfuric acid (96%) Ethanol SD3A	50.00 0.25 49.75	1 hr.+	1 hr.+	Nil	
429	Copolymer T_3 Sulfuric acid (96%) Ethanol SD3A	50.00 0.25 49.75	1 hr.+	1 hr.	Nil	
430	Copolymer T_3	100.0	---	---	Nil	Sprayed with Jet-Pak.
430A	Copolymer T_3 Ethanol SD3A Freon 12	20.0 20.0 60.0	1 hr.	---	Nil	
431	Copolymer T_4	100.0	1 hr.	---	Nil	Sprayed with Jet-Pak.
431A	Copolymer T_4 Ethanol SD3A Freon 12	20.0 20.0 60.0	---	---	Nil	

Note: Acidified dimethyldiethoxysilane contains 0.25% by volume sulfuric acid (96%).

Table IIIA. - Investigation of Acid Catalysts

Formula 2911K-	Composition	Per Cent By Wt.	Rain Spray Life: Pre-flight	Rain Spray Life: Jet Fuel	Rain Spray Life: In-flight Applic.	Comments
353	p-Toluene sulfonic acid Ethanol SD3A	75.0 25.0	1 hr. +	1 hr.	---	Flash point 100°F. (Tag Open Cup)
353A	p-Toluene sulfonic acid Ethanol SD3A	70.0 30.0	1 hr. +	1 hr.	---	Flash point 100°F. (Tag Open Cup)
353B	p-Toluene sulfonic acid Isopropanol 99%	60.0 40.0	1 hr.	---	---	Flash point 90°F. (Tag Open Cup)
353C	p-Toluene sulfonic acid Ethanol SD3A Water	67.5 22.5 10.0	1/2 hr.	---	---	
353D	p-Toluene sulfonic acid Isopropanol 99% Water	54.0 36.0 10.0	1/2 hr.	---	---	

Note: The catalysts were evaluated in conjunction with Formula 2911K-394.

Table IIIB. - Investigation of Alkaline Catalysts

Formula 2911K-	Composition	Per Cent By Volume	Rain Spray Life: Pre-flight	Rain Spray Life: Jet Fuel	Rain Spray Life: In-flight Applic.	Comments
420	Copolymer H Potassium hydroxide (10% in ethanol)	50.0 50.0	Nil			Viscosity increases on ageing.
421	Copolymer H Potassium hydroxide (5% in butanol)	50.0 50.0	Nil			Solution gels on ageing.
422	Dimethyldiethoxysilane Potassium hydroxide (10% in ethanol)	50.0 50.0	Nil			
424	Copolymer H Potassium hydroxide (1% in ethanol)	99.0 1.0	Nil			

Table IIIB. (Cont'd.)

Formula 2911K-	Composition	Per Cent By Volume	Rain Spray Life: Pre-flight	Rain Spray Life: Jet Fuel	Rain Spray Life: In-flight Applic.	Comments
425	Copolymer H Potassium hydroxide (1% in ethanol)	98.0 2.0	Nil			
426	Copolymer H Potassium hydroxide (1% in ethanol)	97.0 3.0	Nil			
427	Copolymer H Potassium hydroxide (1% in ethanol)	95.0 5.0	Nil			